

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant(s):	Edward W. MERRILL <i>et al.</i>	Attorney Docket No: 37697-0062
Serial No.:	10/197,263	Confirmation No.: 5033
Filing Date:	July 18, 2002	Examiner: Susan W. BERMAN
Title:	RADIATION AND MELT TREATED ULTRA HIGH MOLECULAR WEIGHT POLYETHYLENE PROSTHETIC DEVICES	

DECLARATION UNDER 37 C.F.R § 1.131

**THIS DECLARATION IS TO BE MAINTAINED UNDER THE LIMITED ACCESS
PROVISIONS OF 37 CFR § 1.612; MPEP § 2309.03**

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Applicant(s): Edward W. MERRILL *et al.*

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Group Art Unit: 1711

Title: RADIATION AND MELT TREATED ULTRA HIGH MOLECULAR
WEIGHT POLYETHYLENE PROSTHETIC DEVICES

DECLARATION UNDER 37 C.F.R § 1.131

We, Edward W. Merrill, William H. Harris, Premnath Venugopalan, Murali Jasty, Charles R. Bragdon, and Daniel O. O'Connor, do hereby declare as follows:

1. We understand that the claims in the captioned application have been rejected over U. S. patent No. 6,281,264, which lists January 20, 1995 as the earliest filing date.

2. We submit this declaration, based on our personal knowledge to explain the process leading to the inventions disclosed in U. S. application Serial No. 10/197,263 that relate to orthopedic preformed materials and polymers, articles and the like that comprise polymers cross-linked by irradiation and heated to or above the melting point of the polymer, and methods of making same.

3. Wear of polyethylene and the incidence of osteolysis became known during mid-1980's. The realization was that the osteolysis was related to the formation of very small polyethylene particles through wear. In order to improve wear resistance of polyethylene and to prevent the formation of fine polyethylene particles, we carried out inventive activities and designed and carried out various experiments prior to January 20, 1995. All dates on the attached Exhibits have been masked out.

Cross-linking by Irradiation in a Molten State to lower crystallinity and Preserve the Entangled State

4. Prior to January 20, 1995, we developed several ideas to lower crystallinity and preserve the highly disordered entangled state of the ultra-high molecular weight polyethylene (UHMWPE) in order to solve the wear problem (see Exhibit 1). One embodiment that we developed was to cross-link the polyethylene in the molten state by use of irradiation so that the polyethylene could not revert readily to the chain folded state, which was preferred at the time. This embodiment is memorialized in item C of Exhibit 1. The process also is disclosed in U.S. Serial No. 08/600,744, filed February 13, 1996, and issued as U.S. Patent No. 5,879,400 (the '400 patent) (see, for example, Column 6, lines 55-67, and Example 1), U.S. Serial No. 08/726,313 (the '313 application, filed October 2, 1996) (see, for example, page 25, Example 1), and U.S. Serial No. 08/798,638 (the '638 application, filed February 11, 1997) (see, for example, pages 33-34 , Example 1).

5. Prior to January 20, 1995, we conceived of various embodiments of the invention, that is irradiation of UHMWPE combined with melting, as described in item C of Premnath Venugopalan's note (see Exhibit 1). At the time, we believed that a prosthesis formed out of UHMWPE bar stock that had been heated above the melting point and irradiated (in air or an inert environment) in that molten state (see item c), or had been irradiated and then heated above the melting point, would form cross-links (see item b). The increased mobility of the molecules in the molten state allows the free radicals to combine with each other and form cross-links, as opposed to remaining in a trapped state.

6. Prior to January 20, 1995, we continued conducting melt-irradiation (MIR) experiments at Mr. Kenneth Wright's laboratory (the High Voltage Research Laboratory (HVRL), located in building N-10 of M.I.T. at 155 Massachusetts Avenue, Cambridge, MA 02139. Mr. Kenneth Wright was responsible for the day-to-day operation and management of the radiation applications activities of the HVRL, including scheduling, operation, maintenance of equipment and research with the Van de Graaff

accelerators). Six UHMWPE samples were irradiated at 1.0, 2.5, 5, 10, 20 and 50 Mrads by Mr. Ken Wright. The samples were heated to melt and irradiated while in a molten state. Subsequently, MIR experiments using solid bars in sealed containers (sealed glass vials) were done at Mr. Wright's laboratory. Copies of Mr. Wright's laboratory logbook page numbers 122-123 and 126-127 containing the record of MIR work done are attached as Exhibit 2. A copy of the corresponding page 10 of lab book no. 2 is attached as Exhibit 3.

7. Also, prior to January 20, 1995, we conducted a thermal analysis of the irradiated UHMWPE specimens, as described in paragraph 9, by use of DSC. This DSC method is used to determine melting and crystallization temperatures as well as the energy input required to melt and energy output generated during crystallization. The energy required to melt is then used to quantify the degree of crystallinity.

Six polymer samples, as described in paragraph 9, also were irradiated in sealed pans for crystallinity analysis. The samples were heated to melt and irradiated while in a molten state. A copy of Premnath Venugopalan's laboratory note book page numbers 8-9 is attached as Exhibit 3 (see Expt 1 and Expt 2). Thus, prior to January 20, 1995, we have practiced the process of heating polyethylene to a temperature at or above the melting point of polyethylene and irradiating the polyethylene in a molten state. The DSC testing on the polyethylene samples that were irradiated in a molten state was conducted. Crystallinity levels had dropped to 37.77% (printed as 37.8%) for the sample given a 20 Mrad radiation dose. Copies of the corresponding DSC data sheets are attached as Exhibit 4 (marked as 'data-6'). Crystallinity data from unirradiated GUR415 bar stock was used as control. Irradiation dose (20 Mrad), temperature (125.51, printed as 125.5) and crystallinity data (37.77%, printed as 37.8%) from this work are presented in a patent application that became the '400 patent (see, for example, Table 1 on column 9 of the '400 patent), in the '313 application (see, for example, Table 1, page 27), and the '638 application (see, for example, Table 1, page 35).

8. Other tests on melt-irradiated polyethylene, for example, Electron Spin Resonance (ESR), were conducted to determine residual free radicals. Swell Ratios to assess degree of cross-linking also were determined, prior to January 20, 1995, by submerging polyethylene in DecalinTM at 150°C for dissolution of polymeric chains.

ESR results indicated no detectable free radicals in melt-irradiated polyethylene, whereas the control polyethylene that was irradiated at room temperature without concurrent or subsequent melting showed the presence of free radicals. The absence of free radicals in the melt-irradiated polyethylene indicates that any further oxidative degradation would be avoided, and thus the material was suitable for use in medical prostheses. See Exhibit 5 for ESR spectra from an experiment conducted prior to January 20, 1995. The ESR spectra show samples irradiated at room temperature contain free radicals; whereas, the samples irradiated at 175°C do not have any detectable free radicals.

Swell Ratios indicated that the melt-irradiated polyethylene was highly crosslinked and did not allow dissolution of polymeric chains, while unirradiated polyethylene dissolved completely, which signifies lack of cross-linking in the unirradiated polyethylene. See Exhibit 6 for swell test results of an experiment conducted prior to January 20, 1995. Swell test data shows control specimens dissolve completely within 24 hours in DecalinTM at 150°C.

9. The above testing confirmed that we had invented, among other things, (1) methods of making an improved prostheses by combining melting and irradiating to cross-link UHMWPE, and (2) improved prostheses that were the result of these processes. These prostheses are wear resistant and thus would not be a source of the fine particles that would result in bone resorption, as was the case with the prior art conventional UHMWPE prosthesis.

Cross-linking by irradiation at room temperature and subsequent melting

10. Prior to January 20, 1995, we also developed another embodiment to preserve the highly disordered entangled state of the UHMWPE in order to solve the

wear problem (see item b of Exhibit 1). The embodiment involved cross-linking the polyethylene in at room temperature ('cold irradiation') by irradiation and subsequent melting. The process is referred to as Cold-irradiation and Subsequent Melting or "CISM " and is disclosed in U.S. Serial No. 08/726,313 (the '313 application, filed October 2, 1996) (see, for example, page 39, Example 8), and U.S. Serial No. 08/798,638 (the '638 application, filed February 11, 1997) (see, for example, pages 47-48 , Example 8).

11. According to this embodiment, UHMWPE is irradiated at room temperature to cross-link and subsequently the irradiated UHMWPE is heated above the melting point of about 135°C and then cooled. This process subsequently referred to as cold irradiation and subsequent melting or "CISM", meaning irradiation of UHMWPE at about room temperature and then heating the irradiated UHMWPE above the melting point and resolidifying.

12. Prior to January 20, 1995, we had a number of UHMWPE specimens irradiated at room temperature at Mr. Kenneth Wright's laboratory. A copy of Mr. Wright's laboratory logbook pages number 120-121 containing a log of irradiation work done prior to January 20, 1995 is attached as Exhibit 2. The experiment (Marked as Irradiation Experiment 1) and the process including radiation doses used are recorded in lab note book no. 2, page no. 8. A copy of the laboratory note book page number 8, which is attached as Exhibit 3.

13. Prior to January 20, 1995, we conducted a thermal analysis of the room-temperature irradiated UHMWPE specimens, as described in paragraph 11, by use of a testing method called differential scanning calorimetry ("DSC"). This DSC method is used to determine melting and crystallization temperatures as well as the energy input required to melt and energy output generated during crystallization. The energy required to melt is then used to quantify the degree of crystallinity. This DSC method generally has two heating-cooling cycles during which the energy input and output is measured. The cycles include of heating the specimen to a temperature above its melting point, cooling down to room temperature, and heating again to a temperature

above its melting point. The first cycle of this DSC method, involved heating and cooling, was applied to the room temperature irradiated UHMWPE test specimens, as described in paragraph 10 above. Therefore, we practiced the "CISM" process prior to January 20, 1995. The DSC test results indicated that the crystallinity levels decreased from approximately 54.71% present in the starting material to as low as 41.69% when irradiated at 20 Mrad. A copy of that data sheet is attached as Exhibit 4 (see sheet marked as 'data-4') and the corresponding DSC data sheet is attached as Exhibit 4. This reduced crystallinity confirmed our view that the "CISM" method also would improve the structure and wear resistance of the UHMWPE by decreasing the content of chain-folded crystalline lamellae, which otherwise would lead to fibril formation.

The above testing confirmed that we had developed (1) methods of making improved prostheses using the CISM method to cross-link UHMWPE, and (2) improved prostheses that were the result of the process. These prostheses would not be a source of the fine particles that would result in bone resorption as was the case with the prior art UHMWPE prosthesis. Subsequent testing also confirmed that the elimination of free radicals was provided by this method. Thus, prior to January 20, 1995, we conceived and reduced to practice the CISM invention, that is irradiation of UHMWPE at room temperature and subsequent melting, as described in item b of Exhibit 1.

14. The above testing confirmed that we had invented, among other things, (1) methods of making an improved medical implant having bearing surface comprising a solid polyethylene by irradiating to cross-link UHMWPE and subsequent melting, and (2) improved medical implants. This medical implant would be wear resistant and thus would not be a source of the fine particles that would result in bone resorption, as was the case with the prior art conventional UHMWPE prosthesis.

We hereby declare that all statements made herein of our own knowledge are true, and that all statements made on information and belief are believed to be true; and further, that these statements are made with the knowledge that willful false statements, and the like so made, are punishable by fine or imprisonment, or both,

under Section 1001, Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Date

Edward W. Merrill

Date

William H. Harris

Date

Premnath Venugopalan

Date

Murali Jasty

Date

Charles R. Bragdon

5/19/04

Date

Daniel O'Connor

Daniel O. O'Connor

EXHIBIT - 1

BULK CROSS-LINKING FOR IMPROVED UPE PROPERTIES

↳ starting

BASIC MOTIVATION :-

It is clear that as mol. wt. of PE increases, it's abrasion resistance increases. Further as hypothesized by Prof. Merrill, the increase in entanglements should reduce wear. ~~Both~~ ^{there seems to be} ways, an effort at increasing the resistance of PE chains to ~~being~~ ^{being} pulled out of the bulk.

Hence, the following treatments ~~are~~ ^{are} being considered as ways to increase the resistance faced by PE chains against being pulled out:

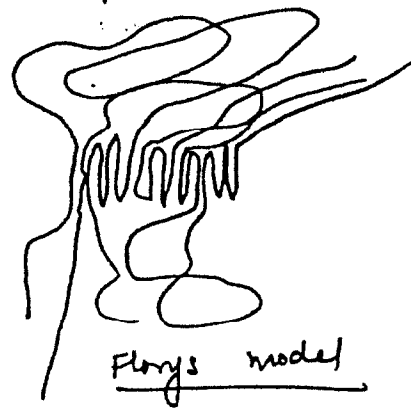
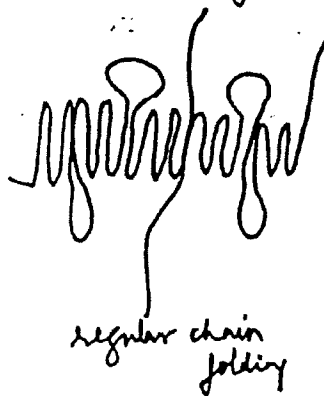
(a) Heat and rapid cooling: Heat the polymer to a completely disordered ~~state~~, highly entangled state and then suddenly cool it ~~in order to~~ in order to trap it in that state.

This may be possible with 10 μ thick films dipped into liq. N₂ but is not possible for larger specimens (Researchers have used several 100 to 100,000 r/min). Further there are problems of differential crystallization at different positions and problem of strain concentrations.

(b) Crosslink as solid, melt, recrystallize: Irradiating the polymer as a solid will mean ~~less~~ ^{concentrated} crosslinking at the crystalline zones but higher crosslinking in the amorphous zones (more mobile chains can ~~also~~ jump more to connect at different places). Melting & recrystallizing these will probably again lead to the original crystal structure ~~with retention~~ (though with reduced crystallinity) ~~though~~ and selective segregation of crosslinks into the amorphous regions. This is expected to be more wear resistant since molecules in the tie regions may be interconnected & crosslinked. Promises to be useful if (a) inter crystalline region slip is

important during wear (to) if loss in hardness is not crucial.

(c) Crosslink as melt, recrystallize: More reduction in crystallinity expected with uniform crosslinking (much more than in x-linking of the solid). More likely that chain-folding in the Flory sense ^{will occur} where ~~chains do not~~ ~~not fold so~~. Instead of one chain folding repeatedly, ~~many~~ many chains will fold in a given region. Hence ~~the~~ the amorphous region will have more interconnected regions, x-link points & longer loops.



(d) Crosslink the solid:

~~the~~ Hardness of original UPE is retained and hopefully there will be ~~more~~ selective crosslinking in the amorphous regions.

Questions/Concerns:

① Degradation vs. Crosslinking
↓
Mol wt ↓
Xtallinity ↑
Wear ↑
Free radicals
(long term existence)

Extent ?

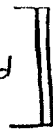
② Crosslinking vs. Crystallinity

↓
decreases as
xlinking ↑ (if recrystallized)

③ Crosslinking vs. Crystal structure

Ideas:

① Crosslinking by irradiation of
Hylamer after it has been processed
and no recrystallization.



⇒ Highest crystallinity
+
Crosslinking.

② Study crosslinking in HDPE instead to see
extent of crosslinking, degradation etc.

IRRADIATED SPECIMENS
FROM ZIMMER

$$* 1 \text{ Mrad} = 10^4 \frac{\text{erg}}{\text{g}} = 10^8 \frac{\text{erg}}{\text{g}}$$

$$\frac{10^{-7} \text{ J}}{10^{-9} \text{ g}} = \text{erg}$$

$$10^{-2} \text{ Gy} = \text{rad}$$

↓

J/kg

$$100 \text{ rad} =$$

$$1 \text{ Gray} = 1 \text{ J/kg} = \frac{10^{17} \text{ erg}}{10^3 \text{ g}}$$

Data 2

DSC RESULTS: Effect of freezer-milling
and Effect of crosslinking by irradiation

Sample	T _{m1} (°C)	T _c (°C)	T _{m2} (°C)	% Cryst 1	% Cryst 2	Difference in Crystallinity	Avg. Lamellar Thickness 1	Avg. Lamellar Thickness 2
(3A) GUR 415 - CONTROL	135.83	122.80	127.52	62.91	46.42	16.49	2.91×10^{-6}	1.51×10^{-6}
(MT1) GUR 415 - FREEZER- MILLED - 10 min.	121.86	154.11	104.47	0.28 <i>See low c type of crystallinity?</i>	0.57 <i>Again low even after heating?</i>	-0.30	1.15×10^{-6}	0.653×10^{-6}
BAR - CONTROL	127.39	121.71	126.57	52.92 <i>Needling compare</i>	46.37	6.55 <i>Graininess</i>	1.52×10^{-6} <i>Increasing</i>	1.44×10^{-6} <i>Decreased of lamellar</i>
BAR - 10 MRad	130.53	123.95	119.05	54.02	45.29	8.73	1.84×10^{-6}	1.02×10^{-6}
BAR - 20 MRad	131.05	128.48	119.78	54.95	41.69	13.26	2.05×10^{-6}	1.05×10^{-6}

EXHIBIT - 2

1.45

COOP COMPUTATION BOOK

NAME	NUMBER
KEN WRIGHT	1

Course F-13-20

Used from _____ to _____

HARVARD COOPERATIVE SOCIETY
1400 MASS. AVE., CAMBRIDGE, MASS. 02138

TECH. COOP
84 MASS. AVE. CAMBRIDGE, MASS. 02139

Polyethylene films George Arnez 1-2 2.5 94 30 340 sec 7.1 1.3 2.5x10⁶ HHH
 mounted on Al Post Hum Sol 37 13 350 10⁶
 plates ~ +0.1 mg 3-27 65 1-2 - - - 10⁶
 2 1/4 hr - - 74 30 1.12w 340 sec - 2.5x10⁶ HHH

Uchu Mukai 1-2 2.8 68 27 - 75 - 1.3 2.5x10⁶ HHH
 3-6478 1-2 2.56 76 30 - - 1.3 2.5x10⁶ HHH

Polyethylene film Jorge Arnez 1,1 2.56 76 30 - 225 sec - 2.5x10⁶ HHH
 mounted on Al " " - - - - -
 1.5 hr 1" Block 1 - - - - 195 - - HHH

3" x 3" in Ambuj. 1-11 2.5 17.6 6.8 1.1 320 1.3 5x10⁶ HHH
 packet 5-16 4 34 13.6 - 250 - 10⁶
 9-16 - - - - 790 - 11
 12-16 - - - - 120 - 1111

Deflex in water Bertrand Schmitt 1-5 2.5 34 13.6 - 165 - 10⁶ HHH
 Solns. H₂O, MUP, Acetone (Humitt) 3-5 - - - - 120 - 11
 6-8 - - - - - - HHH

Ethylene Vinyl Ambuj. 1-6 - - - - 100 - 10⁶ HHH
 Alcohol 2-6 - - - - - - 11
 3-6 - - - - - - 111
 4-6 - - - - - 90 - 111
 5-6 - - - - - - 1111
 6 - - - - - - 11

Aluminum polyethylene * 1-6 - - - - 185 1.3 10⁶ HHH
 mounted on glass slide 1-22 - - - - -
 1-5 - - 50 20.4 - - 1.77x10⁶
 1-10 - - 35 15.2 - 165 - 1.8x10⁶
 1-15 - - 43 17 - 121 - 1.2x10⁶ HHH
 1-20 - - - - - 110 - HHH
 1-25 - - - - - 75 - HHH
 1-30 - - - - - - HHH

Teflon PTFE Bertoni Schmitt 1-7 - 35 13.7 1.1 120 - 10⁶ HHH
 in small dishes no cover
 1" dia. x 3/4" high walls

Polymer Tech Co Merrill 1-9 25 41 15.1 1.1 131 1.3 1.25x10⁶ HHH
 Extrusion of MUP under MUP Schmitt 1-2 - - - - 90 - 111
 1-2 - - - - - -

* #11 $\Sigma 15 \times 10^6$ with overlaps estimate $\sim \frac{180}{500} \Sigma$ (6 sheets $\sim 1/16$ inch)

Turned over

#11 $\Sigma 15 \times 10^6$ with overlaps

2 overlaps, for

$\Sigma 9.5 \times 10^6$

$\Sigma 7.5 \times 10^6$

$\Sigma 7.5 \times 10^6$ (4 overlaps ~ 3 mm)

$\Sigma 15 \times 10^6$ Block turned over

$\Sigma 15 \times 10^6$ Turned over

$\Sigma 10^6$

$\Sigma 2 \times 10^6$

$\Sigma 4 \times 10^6$

$\Sigma 8 \times 10^6$

$\Sigma 5 \times 10^6$ Petri dishes 2-5 2 overlaps

$\Sigma 7 \times 10^6$

$\Sigma 5 \times 10^6$ 2 overlaps

$\Sigma 2 \times 10^6$ 2 overlaps

$\Sigma 4 \times 10^6$

$\Sigma 8 \times 10^6$

$\Sigma 12 \times 10^6$

$\Sigma 16 \times 10^6$

$\Sigma 2 \times 10^6$

$\Sigma 2.2 \times 10^6$

$\Sigma 5 \times 10^6$

$\Sigma 10^6$

$\Sigma 2 \times 10^6$

$\Sigma 5 \times 10^6$

$\Sigma 8 \times 10^6$

$\Sigma 2.5 \times 10^6$ 2 overlaps

$\Sigma 5 \times 10^6$

$\Sigma 5 \times 10^6$ 2 overlaps

Mumill	10	2.5	41	15	1.1	75	1.3	1.25×10^5
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Bertrand	1-2	2.5	39	-	-	90	-	1.25×10^6 11
----------	-----	-----	----	---	---	----	---	-----------------------

PEO collagen Perez	1-9	2.5	62	24	1.1	430	1.3	2x10 ⁶
Collagen on millipore filter	1-6	-	-	-	-	-	-	-

T80 Litho Liquid M2

PMMA	Earl Williams	1	2.5	20	8.1	1.1	40	3.2	2.5×10^5
1/4" dia discs	1/2" thick	2	-	26	10.2	-	-	-	3.8×10^5
		3-5	-	26	-	-	-	-	-
		6-8	-	-	-	-	-	-	-
		9-10	-	17	6.8	-	50	-	2.5×10^5
	1/8" thick	11	2.0	33	10.2	-	90	-	3×10^5
		12-15	-	39	11.9	-	90	-	3.5×10^5

1-3 Goulet	Schmitt	1-18	2.5	39	15	1.1	100	1.3	1.25×10^6
4-9 sch of PEO ² different concentration		1-13	-	-	-	-	-	-	3.2×10^6
		2-8	-	-	-	-	200	-	5.5×10^6 11

Thin Alms Polyurethane		1-3	-	30	12	-	100	1.3	10^6
Mumser Mark 4-6		-	-	-	-	-	-	-	7.25×10^6 11
3-2108, Rm 35-332		-	-	-	-	-	-	-	-

Small (0.5 cm diam) cups	Premnath Venugopal	1-6	2.5	39	15	1.1	75	1.3	1.25×10^6
		2-8	-	-	-	-	-	-	-
		3-6	-	-	-	-	-	-	11
		4-5	-	52	20	-	-	-	111
		5-6	-	63	24	-	-	-	2×10^6 HH
		6	-	-	-	-	-	-	HH
		7	-	-	-	-	-	-	HH
		8	-	-	-	-	-	-	HH

Slush	Tufts. MB. Med. Center	1-4	2.5	33	13.1	-	430	1.3	10^6 11
-------	------------------------	-----	-----	----	------	---	-----	-----	-----------

		5-8	-	-	-	-	-	-	11
--	--	-----	---	---	---	---	---	---	----

		9-12	-	68	27	-	-	-	11
--	--	------	---	----	----	---	---	---	----

		13-16	-	-	-	-	-	-	2×10^6
--	--	-------	---	---	---	---	---	---	-----------------

Various strips	Schmitt	1-6	-	38	15	-	125	-	1.25×10^6
----------------	---------	-----	---	----	----	---	-----	---	--------------------

Core for		7-9	-	-	-	-	-	-	11
----------	--	-----	---	---	---	---	---	---	----

		1-3	-	-	-	-	-	-	-
--	--	-----	---	---	---	---	---	---	---

No overlay (different liquid overlay)

2.25×10^6

Glass cover overlay

Σ Pb over central area

No Pb.

2 overlays

2.25×10^6 #Hatched over

2.5×10^6

Σ

2.25×10^6

2.5×10^6

2.10

2.2×10^7

2.3×10^7

2.4×10^7

2.5×10^7

2.5×10^6

2 overlays

2.5×10^6

2.25×10^6

2.5×10^6

lobes may be slightly less than 5

2.5×10^6

2nd day

2.2×10^6

Turned over for 2nd run

1 discharged

Retri disher \bar{c} glass cover.

2.2×10^6

2.10^7

2.2×10^7

2.5×10^7

2.5×10^7

2.2×10^6

225 1st run hot plate jammed before irradiation - adjusted and passed through

29.8×10^6

219.8×10^6

233.5×10^6

242.8×10^6

22.5×10^6

23.75×10^6

25×10^6

2.10^7

22×10^6

25×10^7

EXHIBIT - 3

Student's Name

Date

8

Subject

Instructor's Name

Irradiation
Studies

→ e beam
at HVRL, MIT.

✓ Kenneth A. Wright.

Student's Name

Date

8

Subject

Instructor's Name

EXPT (1) → Irradiation of solid polymer (UPE) from bar stock

~~Irrad/RT/Air/NOI/UVLT~~
~~PANG~~

Set 1

Set 2

12 samples
of thickness of a
few microns kept
between two slides

6 samples in
DSC pans

RT

1.0 M Rad (each)
2.5 M Rad
5.0 M Rad
10.0 M Rad
20 M Rad
50 M Rad

RT

1.0 M Rad
2.5 M Rad
5.0 M Rad
10.0 M Rad
20.0 M Rad
50.0 M Rad

This was for
studies under
polarizing
microscope
at MGH

DSC Runs done
& results in
the file (#3)

Result → all

showed
spherulites
on melting & cooling
under microscope

EXPT.

(2) Irradiation of barstock while a melt.

9 mg / 1.75C / Air / No follow #T / RANG

FVHT

6 Samples \rightarrow 1.0, 2.5, 5, 10, 20, 50 MRads.at temp. $> 150^\circ\text{C}$

Range (155 to 180°C approx.)

Heating \rightarrow Sample heated ~~approx. once~~ intermittently.Heated \rightarrow 1.0 MRad \rightarrow Heated \rightarrow 2.5 MRad1.0 MRad \leftarrow Heated \leftarrow 5.0 MRad \leftarrow HeatedHeated \rightarrow 20 MRad \rightarrow Heated \rightarrow 35 MRadHeated
50 MRad

Samples placed on a heated Al plate (sink).

Analysis \rightarrow In file #3.DSC Data:Dosemg

1

9.732

2.5

11.433

5

9.540

10

9.061

20

10.133

50

11.638

There was some confusion because the heating exposed the marks on the pans.

Weights were correlated by measuring again.

the weights were well distributed and each far apart from another.

Student's Name

Date

Subject

Instructor's Name

EXPT. 3: Irrad. / 75 C / N₂ atm / NO follow-up H / VIALS
→ FUHT

Samples :- Bare rock (from surface) → constant radius. ~~4~~
Samples by 2.5 to 3 cm radii

4 samples → 2.5, 10, 20, 50 MRad

Method :- Thin strips in vials.

Vial filled with N₂ as in heat treatments.

Heater used this was small enough to fit
under generator outlet
(heater provided by Prof Merrill)

cooling in air (Room temp.)

Sample left in ^{vial with} N₂ atmosphere at RT after irradiation.
for > 5 days

Analysis

Student's Name

10

Subject

Instructor's Name

EXPT 4: Irrad/175C/Air/NO FUHT/VIAL

Samples: Bar stock (b/w 2.5 to 3 cm radial distance)

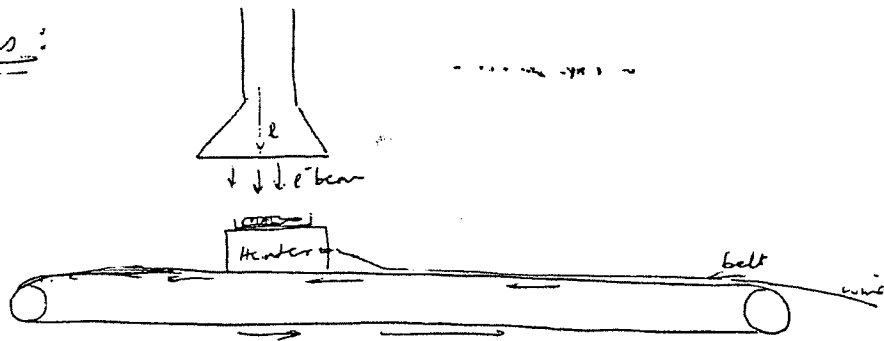
4 Samples \rightarrow 2.5, ^(9.8)~~10~~, ^(19.8)~~20~~, 50 M Rad.

Method: (As in previous page)

Analysis

: E.T9X3

Apparatus:



Student's Name

Date

10

Subject

Instructor's Name

EXPT 5: Irrad / RT / N₂ / NO-FUHT / VIALSample → Same as last page.Method → Same as last page.~~EXPT 5~~

	Dose	
①	2.5	MRad
②	9.8	"
③	18.8	"
④	50	"
⑤		
⑥		

EXHIBIT - 4

E-IRRADIATION OF
THE MELT.

E-IRRADIATION OF THE MELT

Procedural Details:

The following experiment was performed at HVRL, MIT. The Points to be noted ~~steps~~ were as follows:

- (1) Since the hot plate would not fit under the Van de Graaf generator, the specimens ^{in DSC pans} were placed in between two petridishes and laid on a metal plate acting as a heat sink while heating ~~to~~ (supplies heat when placed on the belt).
- (2) The heating was done at intervals ~~between~~ at - - - -

- Start
- After 1.0 MRad
- " 2.5 MRad
- " 5.0 MRad
- " 10.0 MRad
- " 20.0 MRad
- " 30.0 MRad
- After 40.0 MRad

- (3) It can be assumed ~~that~~ that approximately the temperature of the specimens was between 150-200°C

NOTE:

- ① Absence of bimodal distribution during crystallization
→ because no crystals during irradiation,
One phase.
(Scission & X-linking in different ^{crystalline} regions)
- ② ~~Since~~ Since ~~crystalline~~ ^{lamellar} size and crystallinity & T_m decreases,
(significant crosslinking occurring in proportion to scission. (crystal size))
If too much scission compared to crosslinking
⇒ mol wt would decrease
⇒ crystallinity & crystal size will increase
(e.g.) HDPE → 60%.

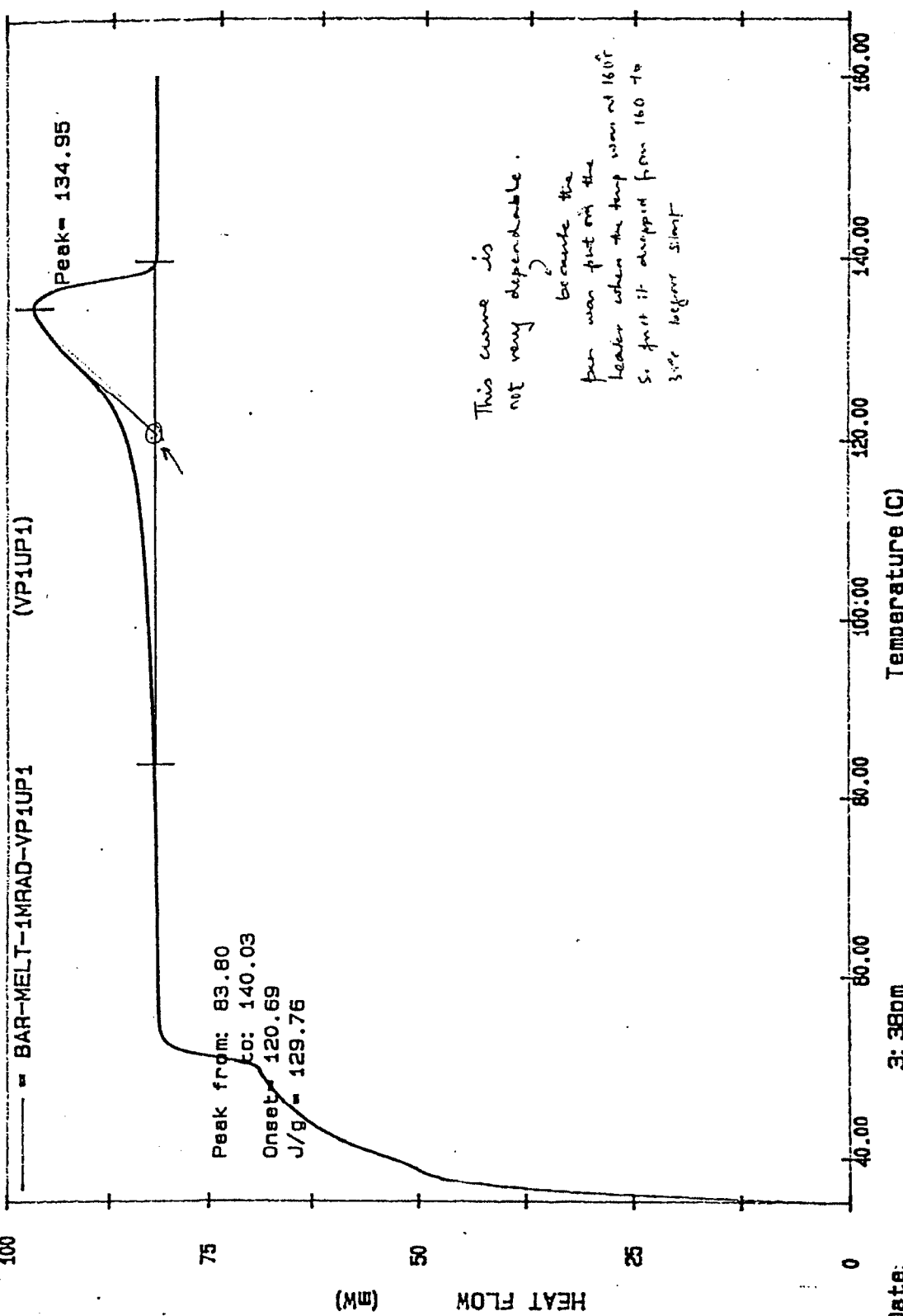
Data 6

Read	Temp (°C)	Cryst thickness (x10 ⁻⁶)	T _c	T _{peak}	T _{m2}	% Cryst 2	Avg lamellar thickness (x10 ⁻⁶)	Cryst. diff.	Remark
✓(1)	100.9	1.10	123.93	122.2	170.6	48.20	1.08	-3.38	
✓(2.5)	100.6	1.11	123.93	118.51	119.23	48.41	1.05	-2.26	
✓(5)	100.6	1.11	121.14	117.69	120.20	45.18	1.07	-1.90	
✓(10)	100.9	1.00	118.95	113.68	118.32	37.27	1.01	2.56	
✓(20)	101.1	0.995	115.06	111.11	117.32	39.09	0.957	-1.31	No second valley during x-radiation
✓(50)	100.8	0.979	105.01	101.18	100.65	32.77	0.748	-1.11	No second valley during x-radiation

NOTE: ① Crystallinity is down below 40% for the first time.
 ② Sudden drop in T_{m2} (as in irradiation of solid P₂) after 20% irradiation (Both T_{m1} & T_{m2}).
 ③ T_{peak} consistent but decreasing as rad. dose increased (Both T_{peak} & T_{peak2}).
 ④ Original Bar Cryst → 55%
 Irrad. melt 4.5% → 30-45%.

Min decrease
at
T_{m1} compared
to
T_{m2}

DATA6



Date: 3: 38pm
Scan rate: 10.0 C/min
Sample Wt: 9.732 mg Path: C: \PE\
File 1: VP1UP1 PREMI

PERKIN-ELMER DSC7

✓
Data 4

Weld	T _{m1} (°C)	T _{peak} (°C)	% Cryst ¹	Arg. thickness (x10 ⁻⁶)	T _c	T _{peak}	T _{m2}	T _{peak}	Cryst ²	Arg. thickness (x10 ⁻⁶)	Cryst. diff.	Remarks
1	128.13	139.47	52.55	1.58	120.38	115.62	123.42	135.05	49.74	1.23	55.7	-
2.77	129.55	138.95	54.83	1.73	120.28	114.61	122.95	133.15	45.14	1.20	9.18	-
5	129.98	139.15	54.44	1.78	120.49	115.16	123.09	131.95	47.18	1.21	7.26	-
10	130.10	139.64	56.20	1.75	119.95	114.90	122.22	131.18	43.95	1.19	6.25	-
20	128.87	139.59	54.71	1.61	124.18	119.5	117.96	130.20	41.69	0.978	13.02	Two overlapping valleys
50	129.01	142.65	57.83	1.67	125.4	118.06	118.15	131.10	44.83	0.985	13.00	Two overlapping valleys

steady OK steady OK steady OK steady OK steady OK steady OK

Weld	T _{m1} (°C)	T _{peak} (°C)	% Cryst ¹	Arg. thickness (x10 ⁻⁶)	T _c	T _{peak}	T _{m2}	T _{peak}	Cryst ²	Arg. thickness (x10 ⁻⁶)	Cryst. diff.	Remarks
0	127.35	136.65	52.92	1.52	121.71	117.19	126.57	134.70	46.37	0.44	6.55	-
8-10	130.53	140.50	54.02	1.89	127.95	120.85	119.05	134.95	45.29	1.02	6.73	-
20	131.95	141.88	54.95	2.05	129.48	122.89	119.78	136.00	41.69	1.05	13.26	-

MISCELLANEOUS DOC DAPPLS

Part #	CRST OFF
132.87	13.83
130.88	28.50
131.87	32.38
132.20	6.24
135.18	27.09
130.28	-5.32
132.40	0.83
132.81	21.40
133.88	3.51
132.20	3.33
138.18	-0.48
138.10	-1.38
131.31	7.22
131.45	1.82
130.83	2.07
130.10	2.88
134.08	18.49
132.55	0.83
138.38	1.12
132.81	4.80
132.82	-1.63
132.13	-1.89
127.71	-0.89
127.22	1.03
128.23	-7.81
132.88	8.82
133.75	-5.27
133.17	-1.24
117.82	-0.30
134.70	6.68
134.83	8.72
128.00	13.28
132.08	-48.72
133.75	5.78
133.88	3.88
131.18	4.35
130.20	13.03
131.10	13.00
135.88	-5.38
135.81	-2.28
132.48	-1.80
130.68	2.88
138.78	-1.31
117.88	-1.11

VP10N1

BAR-MELT-1MRAD-VP10N1

30

22.5

15

7.5

0

HEAT FLOW (mW)

Peak from: 96.35
to: 126.98
Onset= 123.93
J/g --107.30

Peak= 120.27

Shoulder
x-labeled
P1

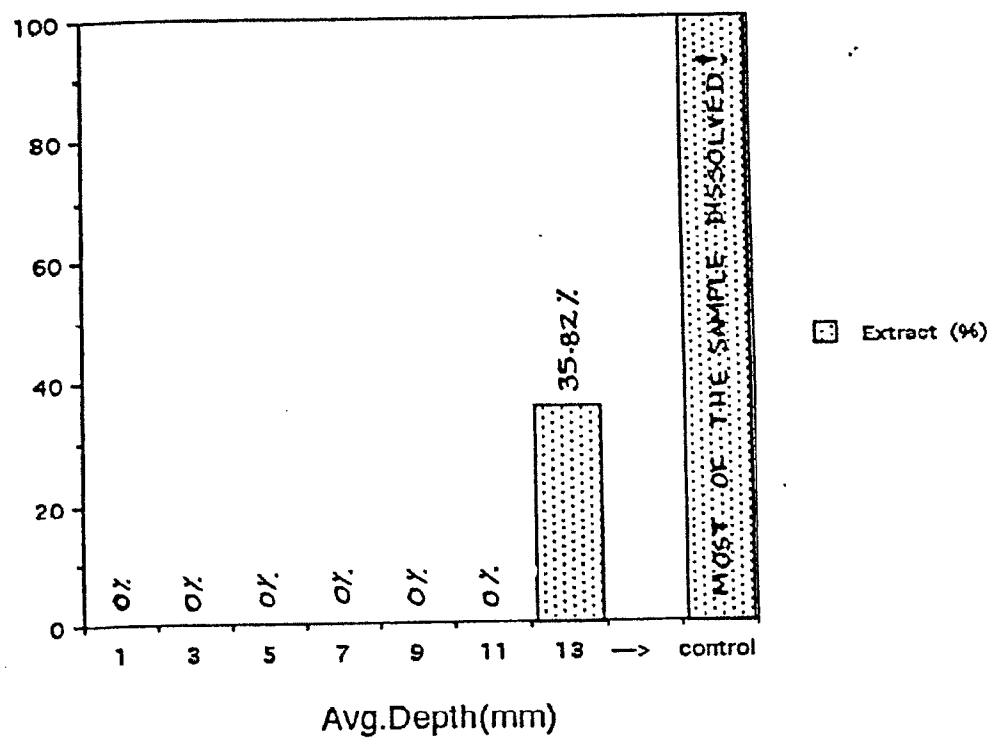
Temperature (C)

Date: 3:54pm
Scanning Rate: -10.0 C/min
Sample Wt: 9.732 mg Path: C:\PE\
File 1: VP10N1 PRENT

PERKIN-ELMER DSC7

EXHIBIT - 5

Extract percent in Decalin at 150 C (Samples from axis of irradiated cup 3)



Results from swelling test in Decalin at 150 C (Samples from axis of irradiated cup 3)

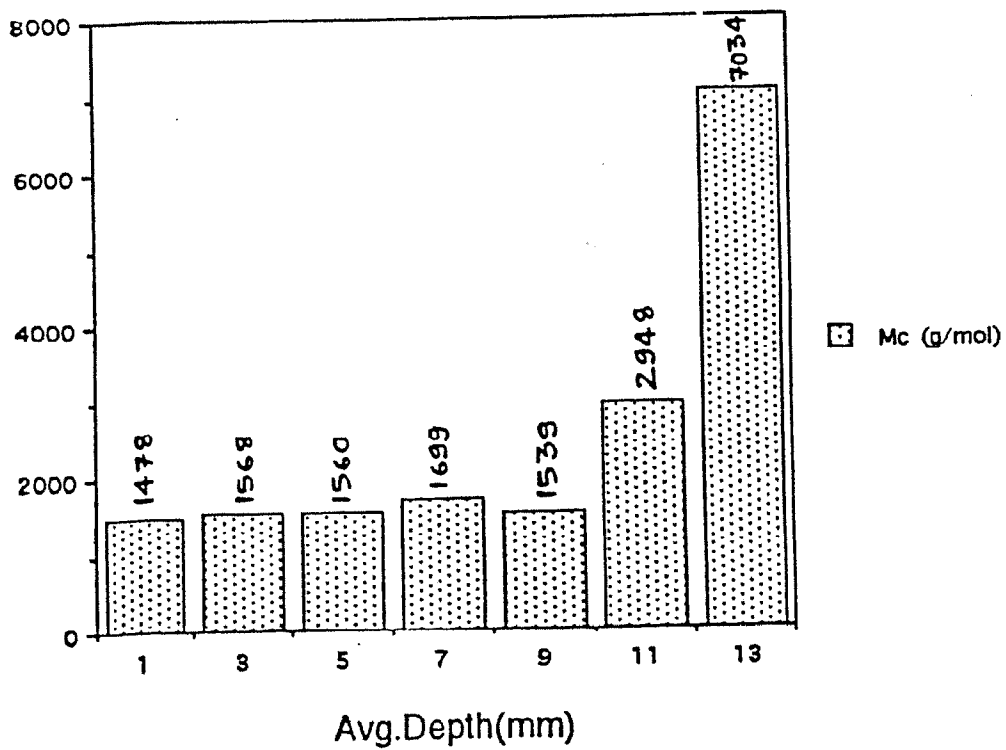
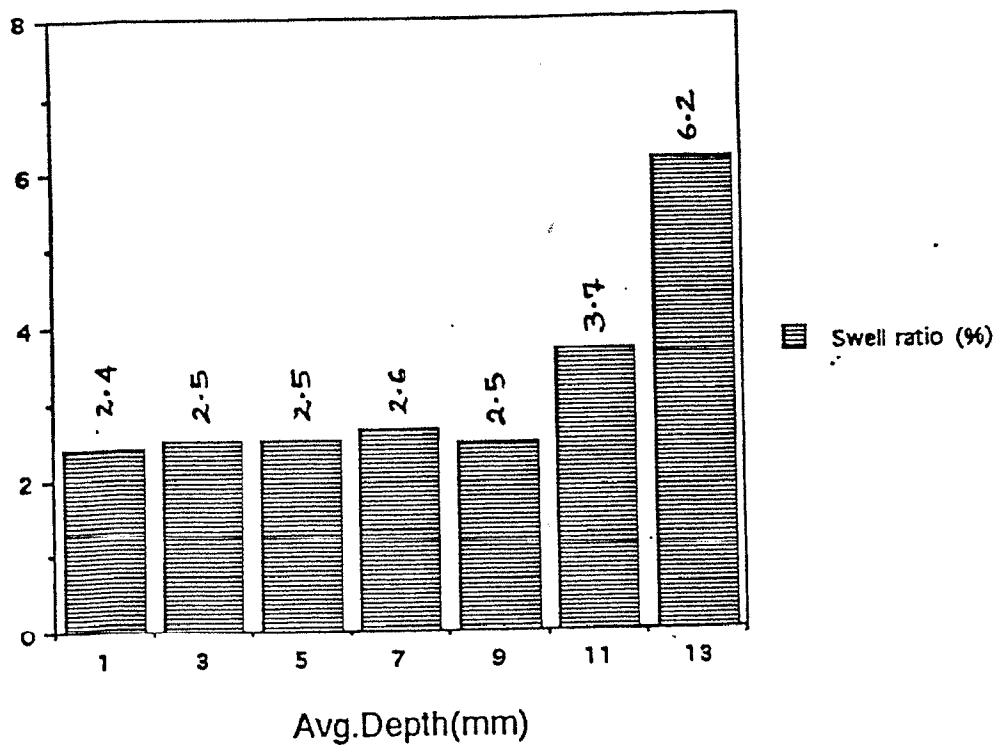


EXHIBIT - 6

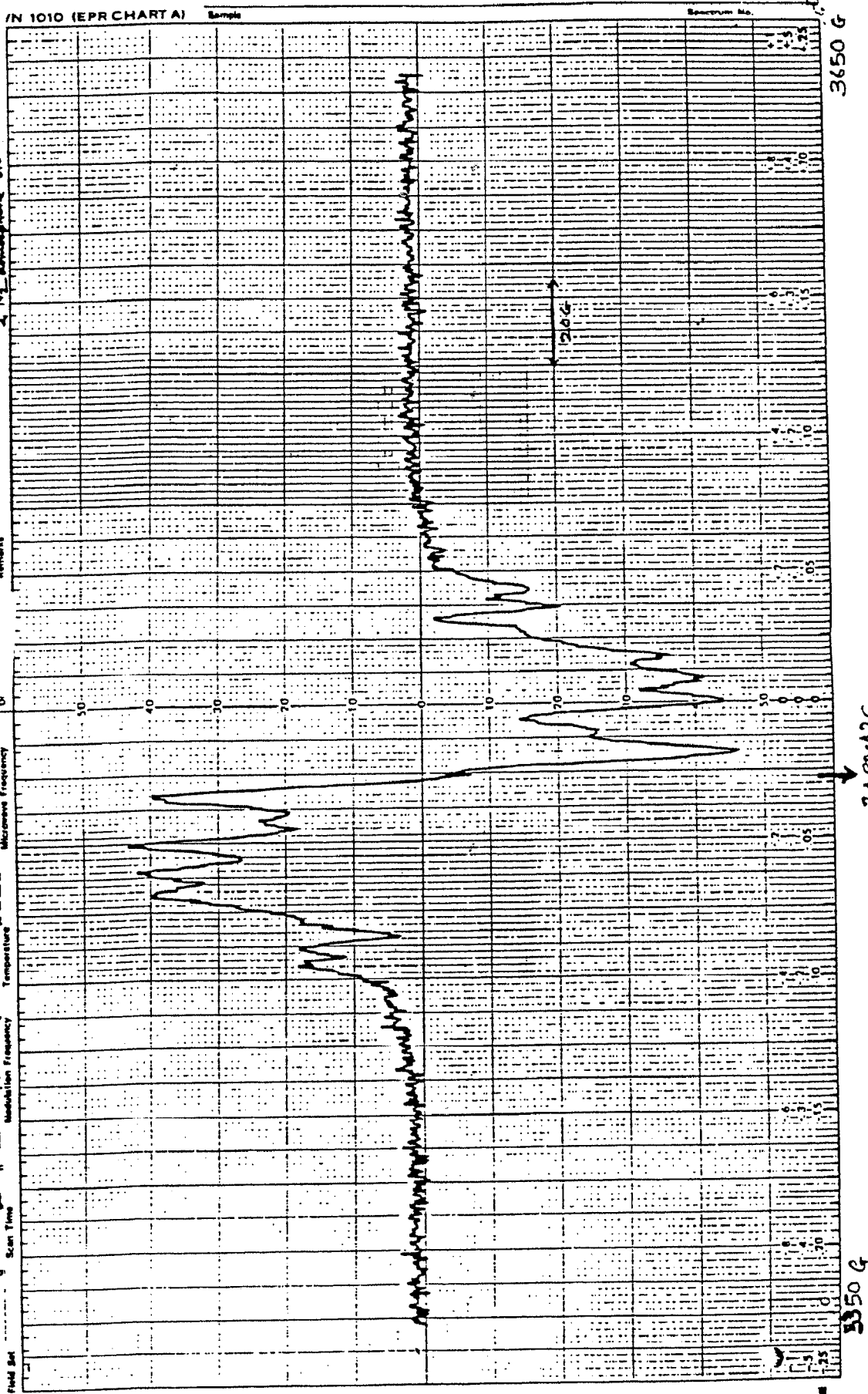
198 Date

Tony Modestino for Remondet

RECORDED CHARTS

Sample: Bar Stock Immersed in Solid at RT
Remarks: N₂ atmosphere on

Field Set 3350 0 3650 0
Time Constant 1.28 msec
Scan Rate 4.156 sec
Modulation Frequency 100 kHz
Modulation Amplitude 3.74×10^{-1} a
Modulation Phase 1 mV
Microwave Power 9.75 GHz
Temperature 9.75 GHz



УДК 62-50:62-50:62-50

Tommy Modelling for Pennmath

Example: low stock/melt spread under NZ on

NAME

Power

104

2

6

10

9. E. G.

3

1.28

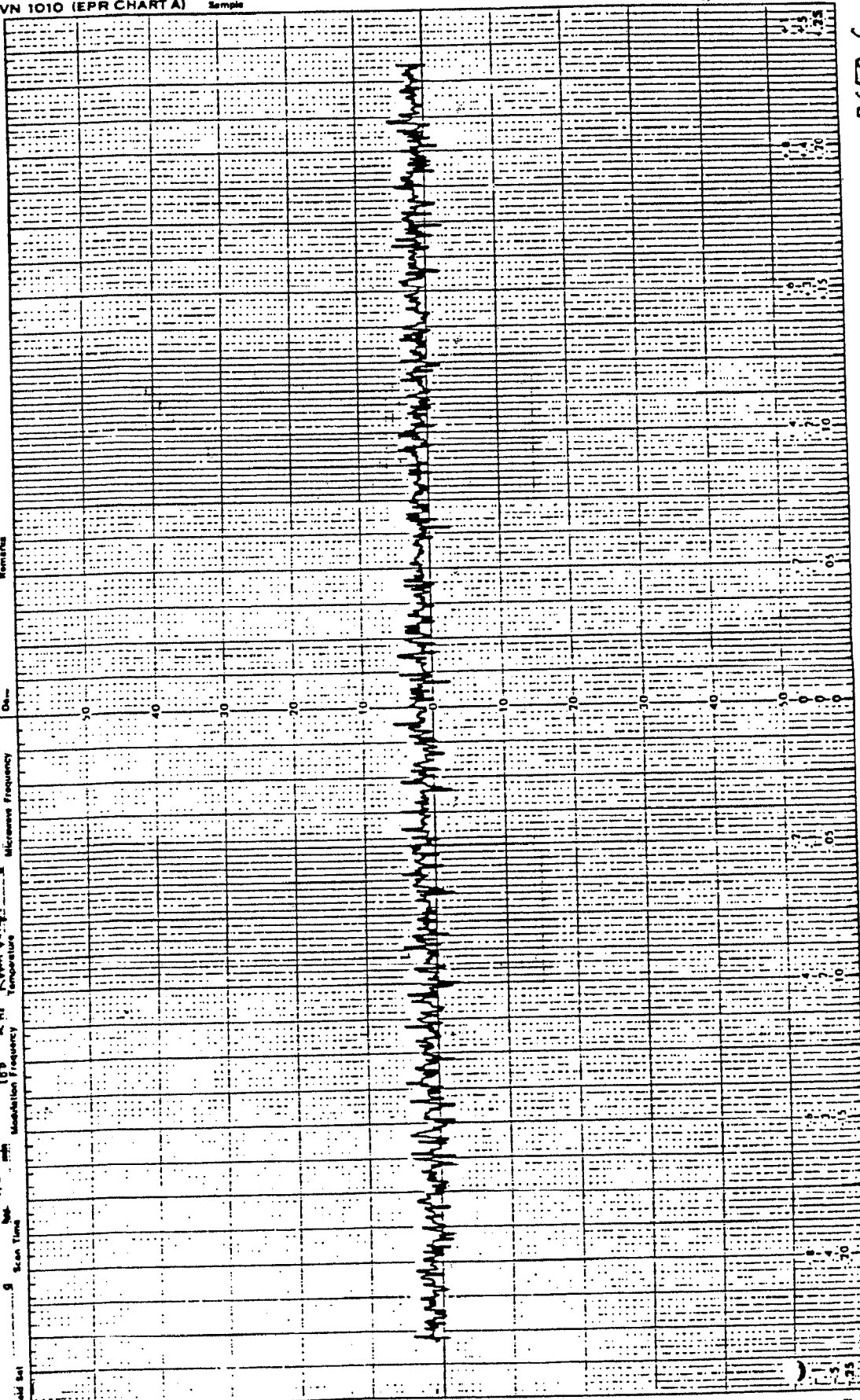
६

2

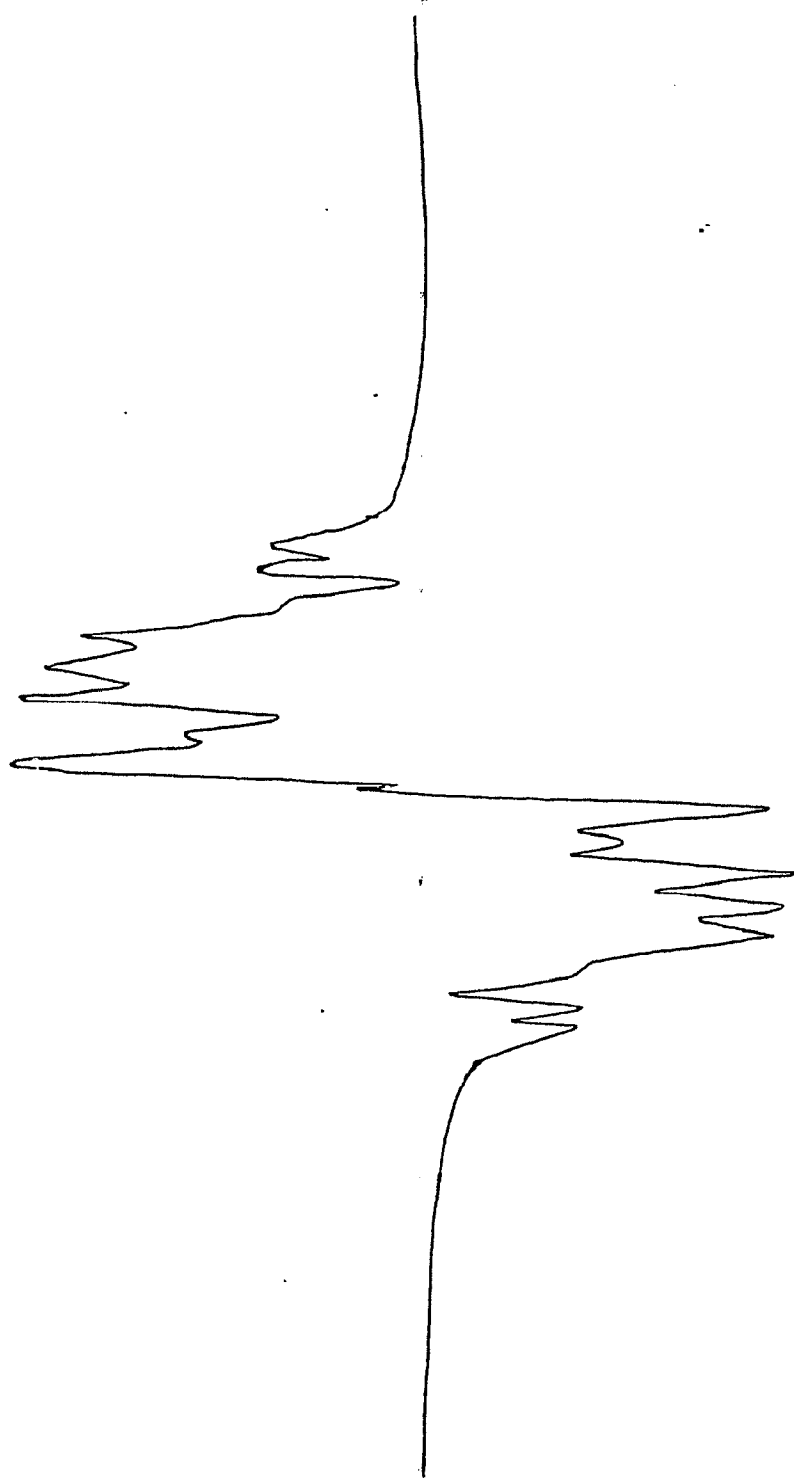
VN 1010 (EPR CHART A)

Sample

Spectrum No.



MIRROR IMAGE OF ESR SPECTRUM OF UHMWPE IRRADIATED AT RT/N₂ ATM.



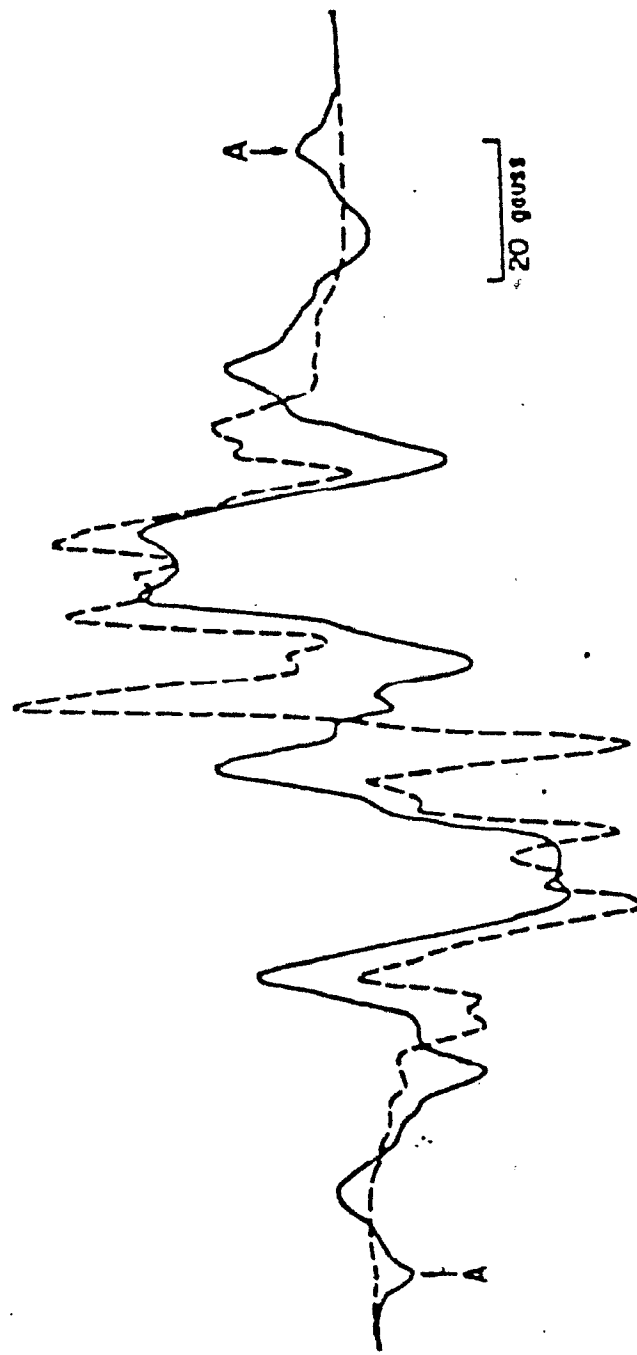


Figure 2. ESR spectra of allyl free radicals (dotted curve) and of mixed alkyl and allyl free radicals after heating to room temperature (solid curve). Decay of alkyl free radicals was calculated from height of peaks marked A.

REFERENCE: D.C. Waterman and M. Dole, J. Phys. Chem., 74(9), 1970, 1913-1922